

Optical brighteners

The present invention relates to novel stilbene derivatives, to a process for the preparation of such compounds and to their use in the optical brightening of textile fibres and paper.

- 5 Sulfonic acid derivatives of bis(triazinylamino)stilbenes are among the most commonly used optical brighteners for paper and textiles.

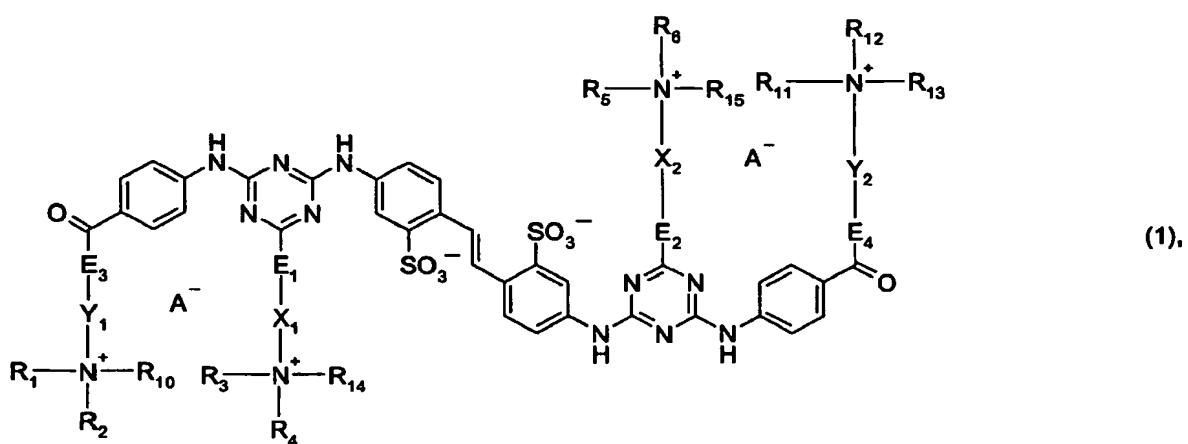
Cationic bis(triazinylamino)stilbenes are frequently used in liquid detergents on account of their compatibility with cationic ingredients. The known cationic stilbene derivatives can be used only to a limited extent, however, in the field of textiles on account of their low substantivity for cellulose.

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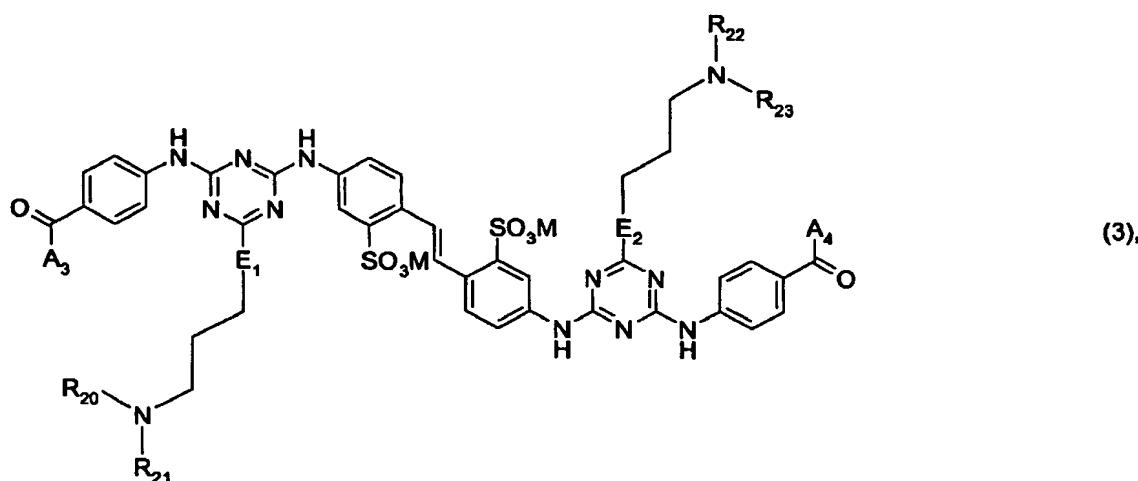
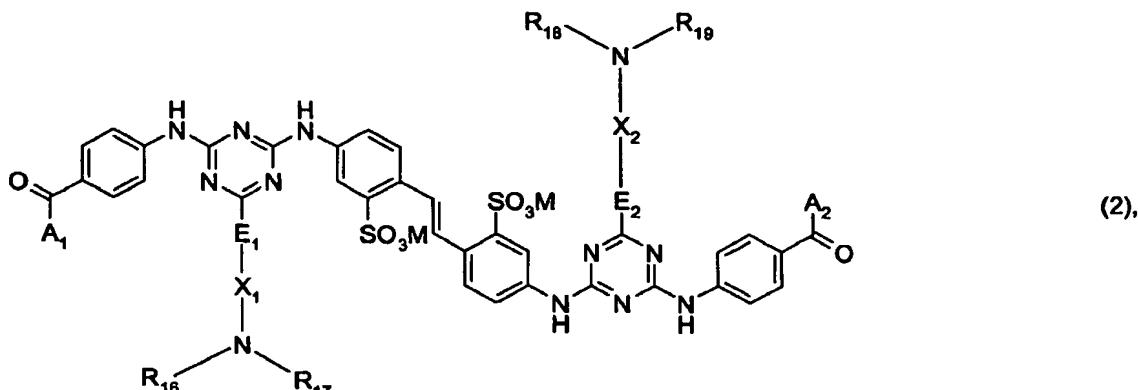
It has now been found that certain amphoteric or cationic bis(triazinylamino)stilbenes exhibit a high brightener action both in paper manufacture and in textile finishing and when used in detergents. The novel compounds exhibit strong absorption in both the UV-A and the UV-B range and have a high degree of substantivity for cellulose.

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The present invention relates to compounds of formula (1), (2) or (3)



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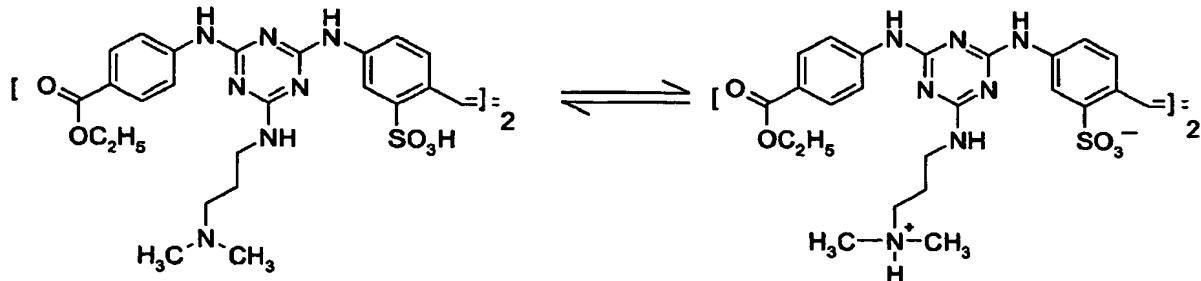
wherein

- 5 M is hydrogen, an alkali metal ion or an ammonium ion,  
 $A_1$  is  $-OR_1$ ,  $-NHR_1$ , N-morpholinyl or 1-piperidyl,  
 $A_2$  is  $-OR_2$ ,  $-NHR_2$ , N-morpholinyl or 1-piperidyl,  
 $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  are each independently of the others  $-O-$ ,  $-NH-$  or  $-NR_9-$ , wherein  $R_9$  together with  $R_4$ ,  $R_8$ ,  $R_2$  or  $R_{12}$  forms an ethylene radical,
- 10  $R_1$  to  $R_6$ ,  $R_{11}$  and  $R_{12}$  are each independently of the others hydrogen, alkyl, alkoxy, aryl, aralkyl, alkoxyalkyl, hydroxyalkyl, aminoalkyl or a group of the formula  $-(C_nH_{2n}Y)_m-R_7$ , wherein Y is  $-O-$ ,  $-NH-$ ,  $-NR_8-$ ,  $-CONH-$  or  $-CONR_8-$ ,  $R_7$  is hydrogen, alkyl or aryl and  $R_8$  is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10, or pairs of two radicals  $R_1$  and  $R_2$ ,  $R_3$  and  $R_4$ ,  $R_5$  and  $R_6$  or  $R_{11}$  and  $R_{12}$  together form a bivalent radical of
- 15 the formula  $-CH_2CH_2OCH_2CH_2-$  or, when  $E_1$ ,  $E_2$ ,  $E_3$  or  $E_4$  is  $-NR_9-$ ,  $R_4$ ,  $R_8$ ,  $R_2$  or  $R_{12}$  together with  $R_9$  forms an ethylene radical,  
 $R_{10}$ ,  $R_{13}$ ,  $R_{14}$  and  $R_{15}$  are each independently of the others alkyl, alkenyl, aryl or aralkyl,

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- X<sub>1</sub> and X<sub>2</sub> are each independently of the other 1,2-cyclohexanediyI, a group of the formula -(C<sub>n</sub>H<sub>2n</sub>)<sub>m</sub>- or a group of the formula -(C<sub>n</sub>H<sub>2n</sub>Y)<sub>m</sub>-, wherein Y is -O-, -NH-, -NR<sub>8</sub>-, -CONH- or -CONR<sub>8</sub>- and R<sub>8</sub> is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10,  
 5 Y<sub>1</sub> and Y<sub>2</sub> are each independently of the other 1,2-cyclohexanediyI, a group of the formula -(C<sub>n</sub>H<sub>2n</sub>)<sub>m</sub>- or a group of the formula -(C<sub>n</sub>H<sub>2n</sub>Y)<sub>m</sub>-, wherein Y is -O-, -NH-, -NR<sub>8</sub>-, -CONH- or -CONR<sub>8</sub>- and R<sub>8</sub> is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10 and A<sup>-</sup> is a singly charged anion or the two A<sup>-</sup> form a doubly charged anion,  
 R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub> and R<sub>19</sub> are each independently of the others hydrogen, 2-hydroxyethyl, 2-aminoethyl or 3-aminopropyl,  
 10 R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> and R<sub>23</sub> are each independently of the others alkyl, and A<sub>3</sub> and A<sub>4</sub> are 2-hydroxyethylamino, 3-dimethylaminopropylamino or 3-diethylaminopropylamino.

The amphoteric compounds of formulae (2) and (3) can be in the form of internal or external salts. For example, when M in formula (3) is hydrogen, the compound of formula (3) can be in the form of a mixture of the neutral compound and the zwitterion in equilibrium:



M in formula (2) and formula (3) can also be an alkali metal cation, such as Na<sup>+</sup> or K<sup>+</sup>, or an 20 unsubstituted or substituted ammonium ion, such as NH<sub>4</sub><sup>+</sup> or N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>.

When any radicals in formula (1), (2) or (3) are alkyl, such radicals are preferably straight-chain or branched C<sub>1</sub>-C<sub>12</sub>alkyl groups. Examples thereof are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, tert-amyl (1,1-dimethylpropyl), 1,1,3,3-tetra-  
 25 methylbutyl, hexyl, 2-methylpentyl, neopentyl, cyclopentyl, cyclohexyl and their respective isomers.

Alkoxy groups are preferably C<sub>1</sub>-C<sub>6</sub>alkoxy groups, for example methoxy, ethoxy, n-propoxy, isopropano, n-butoxy or tert-butoxy.

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Aryl radicals in formula (1) or (2) are preferably unsubstituted or alkyl-substituted C<sub>6</sub>-C<sub>24</sub>aryl, for example phenyl, tolyl, mesityl and isityl.

- 5 Suitable aralkyl groups preferably contain 6-12 carbon atoms. Examples thereof are benzyl and 2-phenylethyl.

Suitable alkoxyalkyl groups are, for example, 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl and 3-ethoxypropyl.

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Examples of hydroxyalkyl are 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-hydroxybutyl, 3-hydroxybutyl and 2-hydroxybutyl.

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Examples of aminoalkyl are 2-aminoethyl, 3-aminopropyl, 2-aminopropyl, 4-aminobutyl, 3-aminobutyl and 2-aminobutyl.

Alkenyl groups as radicals R<sub>10</sub>, R<sub>13</sub>, R<sub>14</sub> or R<sub>15</sub> preferably contain 3-6 carbon atoms, for example allyl, buten-2-yl and penten-2-yl.

20

A<sup>-</sup> in formula (1) is a colourless anion of an inorganic or organic acid. Examples of such anions are halide, such as chloride, bromide or iodide, sulfate, methyl sulfate, tetrafluoroborate, aminosulfonate, perchlorate, carbonate, hydrogen carbonate, benzenesulfonate, naphthalenesulfonate, 4-chlorobenzenesulfonate, oxalate, maleate, acetate, propionate, lactate, succinate, chloroacetate, tartrate, methanesulfonate and benzoate.

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Preferred anions are hydrogen sulfate, sulfate, lactate, acetate and especially chloride and methyl sulfate.

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In a preferred embodiment of the invention, the compounds of formulae (2) and (3) are symmetrical; that is to say preference is given to compounds of formula (2) wherein the substituents A<sub>1</sub> and A<sub>2</sub>, E<sub>1</sub> and E<sub>2</sub>, X<sub>1</sub> and X<sub>2</sub>, R<sub>16</sub> and R<sub>18</sub> and also R<sub>17</sub> and R<sub>19</sub> are in each case identical; and compounds of formula (3) wherein the substituents A<sub>3</sub> and A<sub>4</sub>, E<sub>1</sub> and E<sub>2</sub>, R<sub>20</sub> and R<sub>22</sub> and also R<sub>21</sub> and R<sub>23</sub> are in each case identical.

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Also preferred are compounds of formula (1) wherein the substituents E<sub>1</sub> and E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub>, X<sub>1</sub> and X<sub>2</sub>, Y<sub>1</sub> and Y<sub>2</sub>, R<sub>3</sub> and R<sub>5</sub>, R<sub>4</sub> and R<sub>6</sub>, R<sub>14</sub> and R<sub>15</sub>, R<sub>1</sub> and R<sub>11</sub>, R<sub>2</sub> and R<sub>12</sub> and also R<sub>10</sub> and R<sub>13</sub> are in each case identical.

- 5 In formulae (1) and (2), X<sub>1</sub> and X<sub>2</sub> are preferably ethylene or trimethylene.

In formula (3), R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> and R<sub>23</sub> are preferably methyl or ethyl.

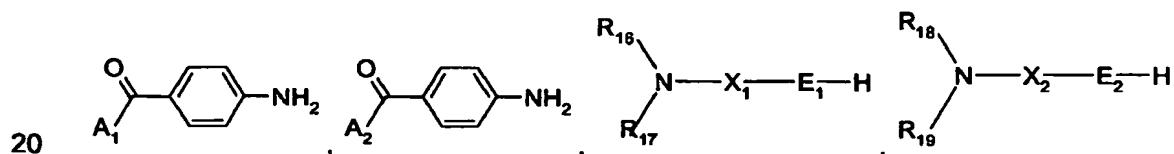
Also preferred are compounds of formula (2) or (3) wherein A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub> are amino,

- 10 methylamino, 2-hydroxyethylamino, 3-dimethylaminopropylamino or ethoxy.

Preference is also given to compounds of formula (1) wherein R<sub>1</sub> to R<sub>6</sub> and R<sub>10</sub> to R<sub>15</sub> are methyl.

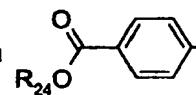
- 15 The compounds of formulae (1), (2) and (3) according to the invention can be synthesised by known methods, starting from cyanuric chloride and 4,4'-diaminostilbene-2,2'-disulfonic acid.

The compounds of formula (2) can be prepared, for example, by reacting cyanuric chloride with, in any order, 4,4'-diaminostilbene-2,2'-disulfonic acid and compounds of formulae

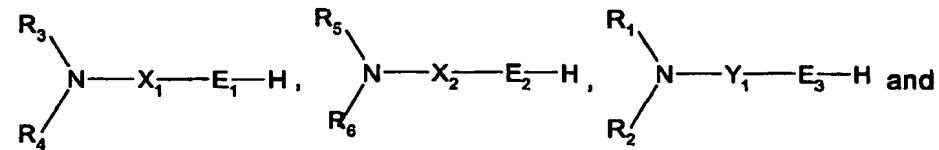


wherein A<sub>1</sub>, A<sub>2</sub>, X<sub>1</sub>, X<sub>2</sub>, E<sub>1</sub>, E<sub>2</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub> and R<sub>19</sub> are as defined above.

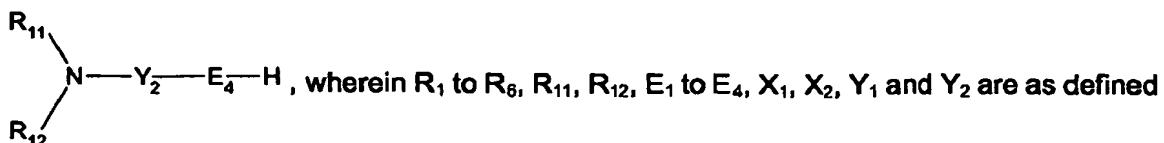
- 25 The compounds of formula (1) can be synthesised analogously, for example by reacting cyanuric chloride first with 4,4'-diaminostilbene-2,2'-disulfonic acid and a compound of

formula  wherein R<sub>24</sub> is alkyl. The intermediate so obtained can then be

reacted, as described e.g. in WO 02/055509, with compounds of formulae



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and then the basic N atoms are quaternised by known methods by reaction with compounds of formulae R<sub>10</sub>-LG, R<sub>13</sub>-LG, R<sub>14</sub>-LG and R<sub>15</sub>-LG, wherein R<sub>10</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub> are as defined above and LG is a leaving group.

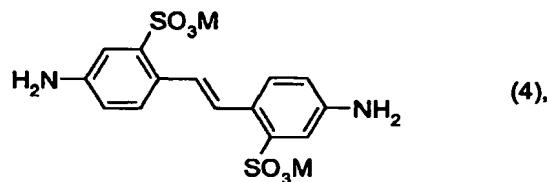
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Suitable compounds of formulae R<sub>10</sub>-LG, R<sub>13</sub>-LG, R<sub>14</sub>-LG and R<sub>15</sub>-LG are *inter alia* the customary alkylating agents known to the person skilled in the art. Examples thereof are alkyl or allyl halides, such as methyl iodide or allyl chloride, dialkyl sulfates, such as dimethyl sulfate or diethyl sulfate, or sulfonic acid esters, such as methyl tosylate or methyl brosylate.

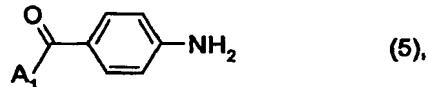
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The starting compounds, the reaction conditions and the methods of separating and purifying the products are known to the person skilled in the art.

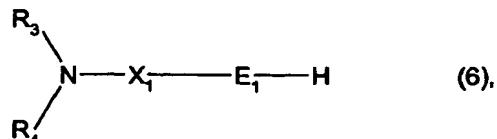
15 The invention relates also to a process for the preparation of symmetrical compounds of formula (2), which process comprises reacting cyanuric chloride by known methods with, in succession in any order, a compound of formula (4)



20 a compound of formula (5)



and a compound of formula (6)



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wherein M, A<sub>1</sub>, E<sub>1</sub>, X<sub>1</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined above.

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The symmetrical compounds of formula (2) obtained by that process can readily be converted into symmetrical compounds of formula (1) by reaction with the corresponding amines and subsequent quaternisation.

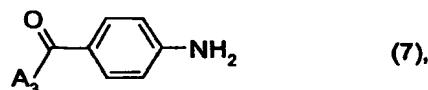
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The present invention relates also to a process for the preparation of symmetrical compounds of formula (3), which process comprises reacting cyanuric chloride by known methods with, in succession in any order, a compound of formula (4)

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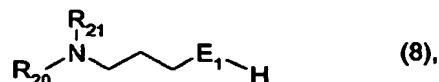


a compound of formula (7)



15

and a compound of formula (8)



wherein M, A<sub>3</sub>, E<sub>1</sub>, R<sub>20</sub> and R<sub>21</sub> are as defined above.

20

A further aspect of the invention relates to a composition for brightening synthetic or natural organic materials, comprising water, a compound of formula (1), (2) or (3) and optionally further adjuvants.

25

Such brightener compositions preferably comprise water and, based on the total weight of the formulation, 3 – 25 % by weight, especially 5 – 15 % by weight, of a brightener of formula (1) or (2) and 0 – 60 % by weight, especially 5 – 50 % by weight, adjuvants.

Suitable adjuvants are, for example, anionic or non-ionic dispersants, such as ethylene oxide adducts of fatty alcohols, higher fatty acids, alkyl phenols, ethylenediamine-ethylene

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oxide/propylene oxide adducts, N-vinylpyrrolidone/3-vinylpropionic acid copolymers, water retention agents, such as ethylene glycol, glycerol or sorbitol, or biocides.

5 The compounds of formulae (1), (2) and (3) according to the invention are especially suitable  
for the optical brightening of natural, semi-synthetic or synthetic textile fibres or of paper.

The novel bis(triazinylamino)stilbenes are preferably used for the treatment of textile fibre  
materials, because, by virtue of their high absorption capacity in both the UV-A and the UV-B  
range, there is obtained not only an excellent brightener action but also a considerable  
10 increase in the sun-protection factor (SPF).

The invention therefore relates also to a method of increasing the SPF of a textile fibre  
material, which comprises treating the textile fibre material with 0.05 – 3.0 % by weight,  
based on the weight of the textile fibre material, of one or more compounds of formula (1), (2)  
15 or (3).

The textile fibres which can be treated in accordance with the method of the invention can be  
natural or synthetic fibres and mixtures thereof. Examples of natural fibres are vegetable  
fibres, such as cotton, viscose, flax, rayon or linen, and animal fibres, such as wool, mohair,  
20 cashmere, angora and silk. Synthetic fibres are, for example, polyester, polyamide and  
polyacrylonitrile fibres. Preferred textile fibres are cotton, polyamide and wool fibres.

The textile fibres to be treated preferably have a density of less than 200 g/cm<sup>2</sup> and have not  
previously been dyed in dark shades.

25 Depending upon the compound of formula (1), (2) or (3) used, the treatment can advantageously be carried out in a neutral, acid or alkaline bath. The method is normally carried out  
in a temperature range of 20°C – 140°C, for example at or close to the boiling point of the  
aqueous bath, e.g. at about 90°C.

30 The application of the optical brighteners, optionally in combination with the application of  
dyes, can be carried out by conventional methods known from textile dyeing, for example the  
exhaust process or the pad-dyeing process.

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When the method according to the invention is combined with a textile treatment or textile finishing process, such a combined treatment can advantageously be carried out using suitable stable preparations that comprise the compound of formula (1), (2) or (3) in a concentration such that the desired SPF improvement is achieved.

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In certain cases, the compounds of formula (1), (2) or (3) can be rendered fully active by an after-treatment. Such an after-treatment may be a chemical treatment, such as treatment with an acid, a thermal treatment or a combined chemical/thermal treatment.

- 10 The compounds of formula (1), (2) or (3) can advantageously be used in admixture with an extender, such as anhydrous sodium sulfate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , NaCl,  $\text{Na}_2\text{CO}_3$ , an alkali metal phosphate, such as sodium or potassium orthophosphate, sodium or potassium pyro-phosphate or sodium or potassium tripolyphosphate.
- 15 In addition to the compounds of formula (1), (2) or (3), the brightener mixtures according to the invention may comprise customary additives. Examples of such additives are emulsifiers, perfumes, colorants, opacifiers, further fluorescent whiteners, bactericides, non-ionic surfactants, fabric-care constituents, especially fabric conditioners, dirt-loosening or dirt-repellent constituents, water-proofing agents, anti-gelling agents, such as nitrites or nitrates of alkali metals, especially sodium nitrate, and corrosion inhibitors, such as sodium silicate.
- 20

The amount of each of those additives is preferably < 2% and is especially in the range of 0.01 – 1.0 %, based on the weight of the fibres being treated.

- 25 The treatment method according to the invention can also be carried out by washing the textile fibre material with a detergent that comprises at least one compound of formula (1), (2) or (3).

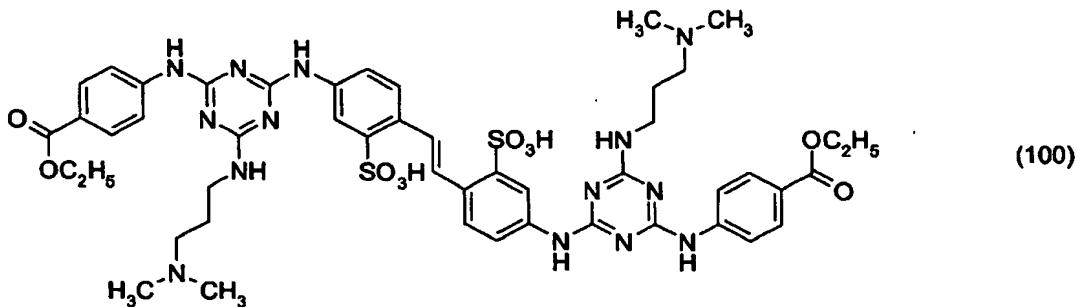
The following Examples illustrate the invention.

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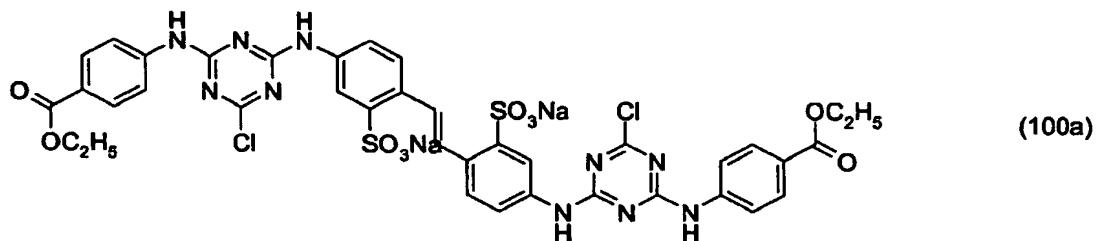
## I. Preparation Examples

### I.1. Compound of formula (100)



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### (a) Intermediate of formula (100a)



- 400 g of ice-water and 120 g (0.65 mol) of cyanuric chloride dissolved in 753 g of methyl  
 10 ethyl ketone are introduced into a 2.5 litre flat-flanged flask. Then, in the course of 70 min,  
 990 ml of a 12 % solution of 4,4'-diaminostilbene-2,2'-disulfonic acid in soda water are slowly  
 added dropwise at pH 4.5-5.0 so that no excess of disulfonic acid is formed. When the  
 addition is complete, stirring is carried out for 10 min at an internal temperature of 5-10°C.  
 15 107.3 g (0.65 mol) of 4-aminobenzoic acid ethyl ester are then introduced into the resulting  
 yellow-brown suspension in the course of 10 min at 5-20°C and pH 7.0-7.5.  
 The yellow suspension is heated to 72°C; after half an hour, 11 ml of 50 % NaOH and after a  
 further half an hour 47 ml of 50 % NaOH are added. After 1.5 hours' stirring at 72°C, a further  
 20 2.5 g (0.015 mol) of 4-aminobenzoic acid ethyl ester are added. After a further one hour's  
 stirring at 72°C, the mixture is allowed to cool. After being left to stand overnight, the reaction  
 mixture is heated to 50°C and filtered through a suction filter. The filter cake is washed with  
 5 % NaCl solution, taken up in 2 litres of ethanol and stirred for 2 h. After leaving to stand  
 overnight, the precipitate is filtered off, washed with ethanol and acetone and dried *in vacuo*  
 at 80°C, yielding 305.4 g (97.24 %) of yellow crystals of the intermediate (100a), which  
 discolour in air.

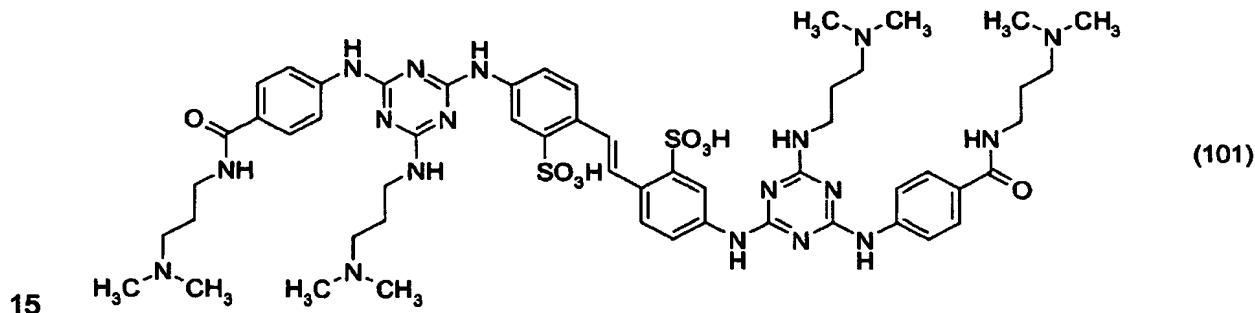
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(b) Compound of formula (100)

32.0 g (0.31 mol) of 3-dimethylamino-1-propylamine are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter. At 50°C, 19.34 g (0.02 mol) of the intermediate of formula (100a) are introduced. The mixture is then stirred for 3 h at 50-55°C, during which time the yellow suspension becomes a solution. The mixture is then heated for 3 h at 60°C. The mixture is then heated to 70°C and stirred for 1.5 h. After being cooled to RT (room temperature), the mixture is diluted with 25 ml of water, and the clear solution is left to stand overnight. The solution is then diluted with water and adjusted to pH 1 with conc. hydrochloric acid. The precipitate is filtered off with suction, taken up in 5 % NaCl solution, filtered again at pH 4 and washed with 5 % NaCl solution and then dried *in vacuo* at 70°C.

Yield: 21.6 g

I.2. Compound of formula (101)

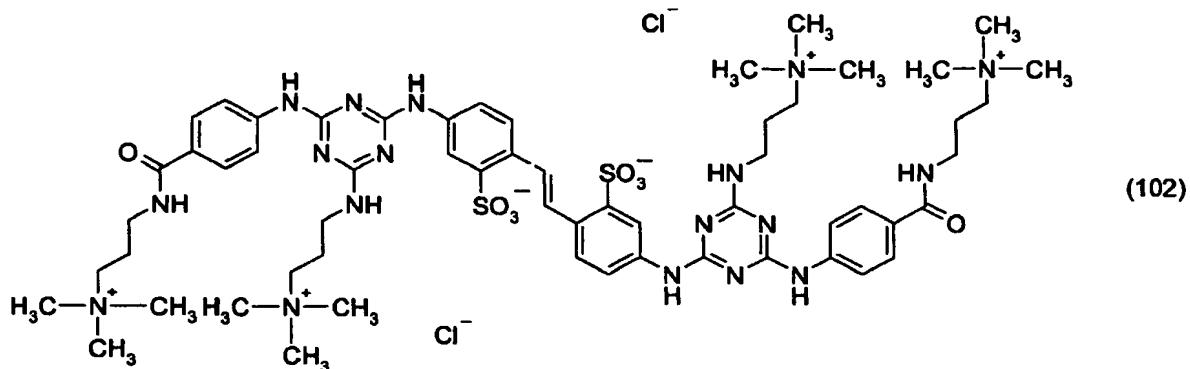


32.0 g (0.31 mol) of 3-dimethylamino-1-propylamine are introduced into a 100 ml sulfonation flask equipped with a condenser. At 60°C, 19.3 g (0.02 mol) of the intermediate of formula (100a) are introduced. The mixture is boiled under reflux (122-125°C) for 24 h. After cooling to RT, the crude product is diluted with water and concentrated using a rotary evaporator. That process is repeated twice. The pH is then adjusted to 8.0 and the supernatant solution is poured off. The residue is suspended in 5 % NaCl solution and acetone and stirred for 1 h. The precipitate is filtered off with suction, again taken up in acetone, filtered and washed with acetone. The crystals so obtained are dried *in vacuo* at 70°C.

Yield: 20.2 g (87 %)

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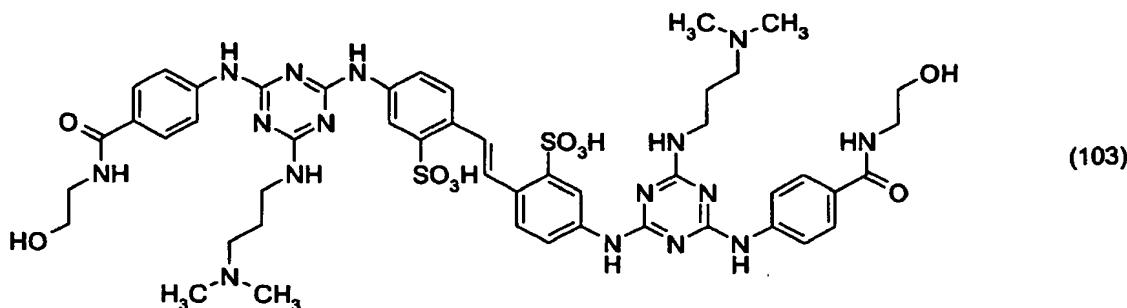
### I.3. Compound of formula (102)



50 ml of water and 40 ml of 2N NaOH are heated at 70°C in a 350 ml sulfonation flask.

- 5 10.0 g (8 mmol) of the compound of formula (101) prepared according to Example I.2 are added, there being formed initially a yellow solution, then a two-phase mixture. After cooling to 40°C, 8.0 g (0.064 mol) of dimethyl sulfate are added dropwise. The mixture is stirred for 2 h at 50°C; then 10 ml of 2N NaOH and 2.0 g (0.016 mmol) of dimethyl sulfate are added. After being stirred for a further 2.5 h at 50°C, the mixture is heated to 75°C in order to
- 10 destroy excess dimethyl sulfate. After cooling to RT and leaving to stand overnight, the supernatant solution is poured off, and the residue is suspended in 10 % NaCl solution. The pH is adjusted to 8-9, the supernatant solution is poured off and the residue is again suspended in 10 % NaCl solution. The solid is separated off in a centrifuge and dried *in vacuo* at 70°C.
- 15 Yield: 9.4 g (90 %).

### I.4. Compound of formula (103)



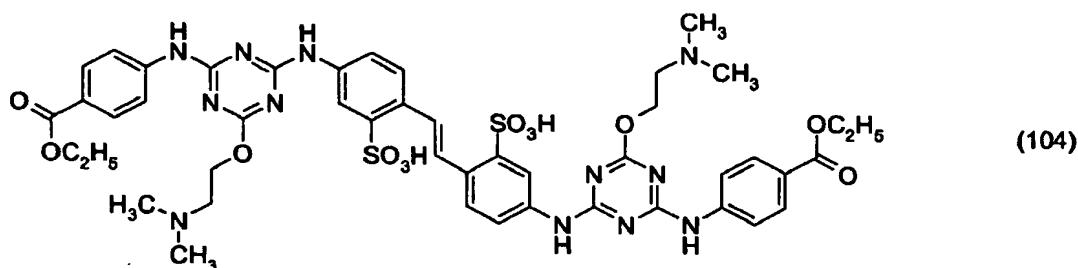
- 20 20 g (0.327 mol) of ethanolamine are heated at 50°C in a 100 ml sulfonation flask equipped with a condenser and pH meter. 10.5 g (0.01 mol) of the compound of formula (100) prep-

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ared according to Example I.1 are introduced in very small portions. The mixture is stirred for 5 h at 120°C and left to stand overnight. After addition of 50 ml of water, firstly a yellow solution and after a few minutes a two-phase mixture is obtained. The water is poured off and the residue is again suspended in water at pH 6. The yellow precipitate is filtered off and washed with 5 % NaCl solution. The residue is taken up in 5 % NaCl solution and stirred at pH 6.0-6.5. The yellow crystals are filtered off, washed again with 5 % NaCl solution and dried *in vacuo* at 70°C.

Yield: 7.7 g (71 %)

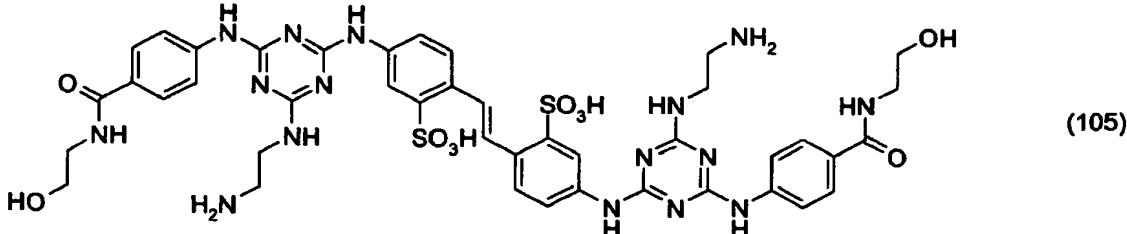
10 I.5. Compound of formula (104)



In a 350 ml sulfonation flask equipped with a condenser and pH meter, 75 g (0.84 mol) of 2-dimethylaminoethanol are heated at 45°C. 21.7 g (0.022 mol) of intermediate of formula (100a), prepared according to Example I.1, are introduced and the mixture is stirred for 1 h at 70°C. After being cooled to RT, the reaction mixture is poured into 300 ml of acetone. The light-yellow supernatant solution is poured off and the residue is again taken up in 300 ml of acetone. The now colourless supernatant solution is decanted off, and the residue is filtered, washed with acetone and suspended in 250 ml of water. After 30 minutes' stirring at pH 5.5, the light-yellow crystals are filtered off, washed with water and dried *in vacuo* at 70°C.

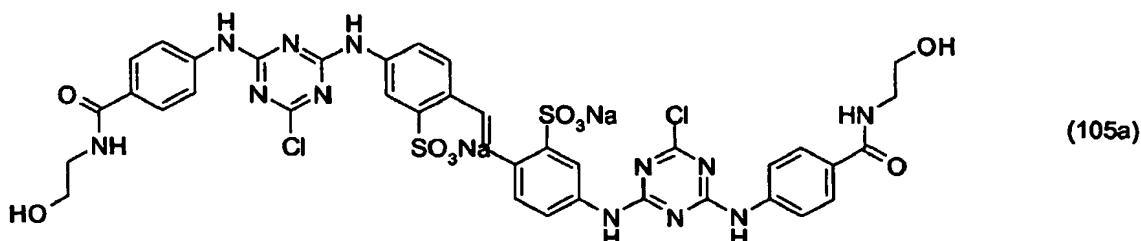
Yield: 19.0 g (84 %)

I.6. Compound of formula (105)



- 14 -

(a) Intermediate of formula (105a)



- 5 200 g of ice-water and 60 g (0.325 mol) of cyanuric chloride dissolved in 465 ml of methyl ethyl ketone are introduced into a 2.5 litre flat-flanged flask. Then, in the course of 40 min, 493 ml of a 12 % solution of 4,4'-diaminostilbene-2,2'-disulfonic acid in soda water are slowly added dropwise at pH 4.5-5.0 so that no excess of disulfonic acid is formed. When the addition is complete, stirring is carried out for 10 min at an internal temperature of 5-10°C.
- 10 Using a metering pump, the suspension so obtained is added dropwise in the course of 35 min at 55-60°C and pH 7.0-7.5 to a solution of 61.5 g (0.341 mol) of 4-amino-N-(2-hydroxyethyl)benzamide in 450 ml of water. The mixture is then stirred for 1 h at 60°C and the methyl ethyl ketone is distilled off at 90°C. After cooling to 70°C, the yellow crystals are filtered through a suction filter, washed with 2.5 % NaCl solution and dried *in vacuo* at 70°C.
- 15 Yield: 144.6 g

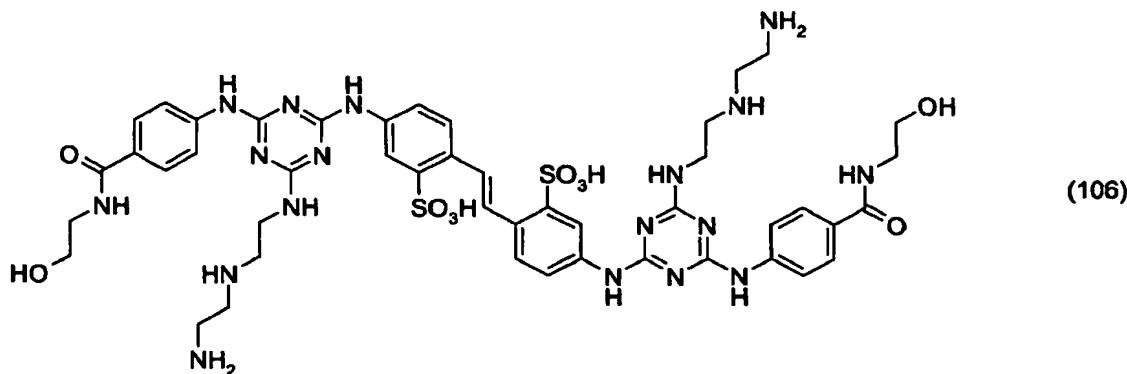
(b) Compound of formula (105)

- 25.3 g (0.42 mol) of ethylenediamine in 150 ml water and 150 ml dioxane are introduced into a 750 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 35.0 g (0.035 mol) of the intermediate of formula (105a) are introduced. The yellow solution is stirred for 1 h at 86-88°C. After being cooled to 70°C, the solution is then diluted with 100 ml of water and adjusted to pH 4.0 with 75 ml of conc. hydrochloric acid. Stirring is continued for a further 1 h at 70°C. The precipitate is filtered through a suction filter and washed with a small amount of water. The filter cake is again suspended in 500 ml of water and dissolved at
- 25 70°C and pH 10.9. The pH is then adjusted to 3.5 with conc. hydrochloric acid. The yellow crystals are filtered through a suction filter, washed three times with 5 % NaCl solution and dried *in vacuo* at 70°C.

Yield: 36.7 g

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**I.7. Compound of formula (106)**



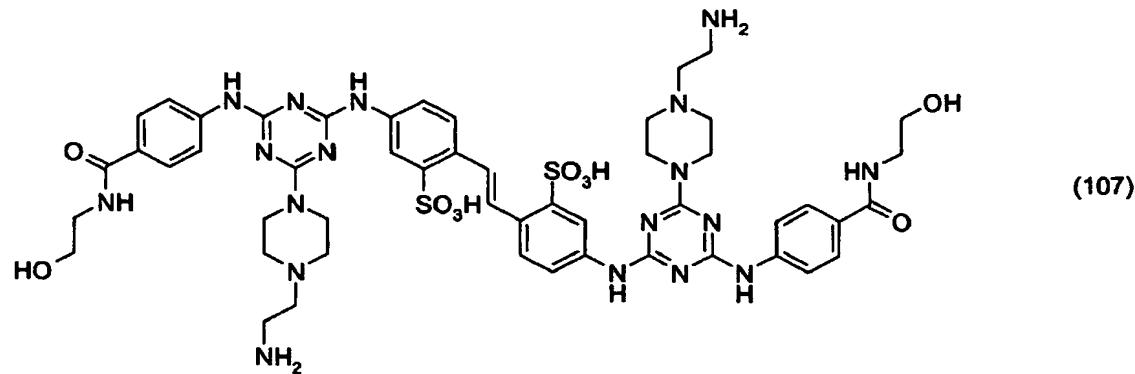
36.2 g (0.35 mol) of diethylenetriamine in 150 ml water and 150 ml of dioxane are introduced

- 5 into a 750 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 35.0 g (0.035 mol) of the intermediate of formula (105a) prepared according to Example I.6 are introduced. The yellow solution is stirred for 3.5 h at 86-88°C. After cooling to 70°C, the solution is then diluted with 100 ml of water and adjusted to pH 4.5 with 115 ml of conc. hydrochloric acid. After being cooled to RT, the mixture is stirred for a further 1 h. The
- 10 precipitate is filtered through a suction filter and washed three times with 2.5 % NaCl solution. The filter cake is again suspended in 500 ml of water. After adjustment to pH 5.3, the yellow crystals are filtered through a suction filter, washed with 2.5 % NaCl solution and dried *in vacuo* at 70°C.

Yield: 32.8 g (81 %)

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**I.8. Compound of formula (107)**

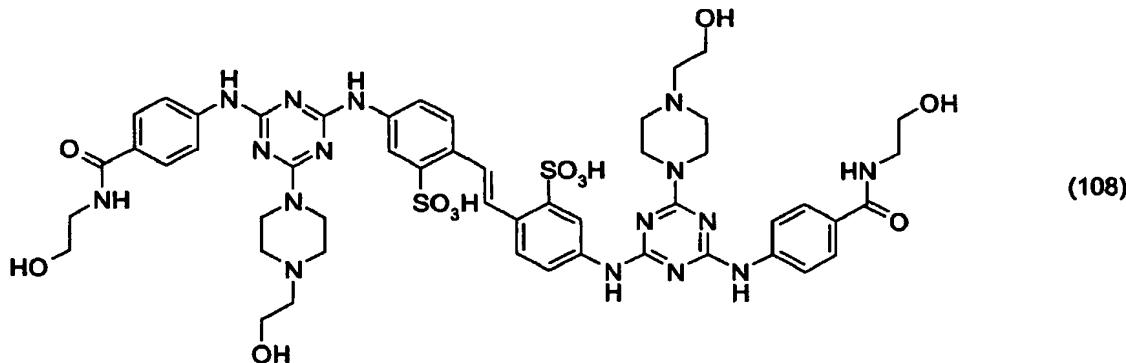


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43.0 g (0.33 mol) of 1-(2-aminoethyl)-piperazine in 150 ml of water and 150 ml of dioxane are introduced into a 750 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 35.0 g (0.035 mol) of the intermediate of formula (105a) prepared according to Example I.6 are introduced. The yellow solution is stirred for 2 h at 86-88°C. After being  
 5 cooled to 70°C, the solution is then diluted with 100 ml of water and adjusted to pH 4.0 with 65 ml of conc. hydrochloric acid. After being cooled to RT, the mixture is stirred for a further 1 h. The precipitate is filtered through a suction filter and washed with water. The filter cake is again suspended in 120 ml of water and 50 ml of 5 % NaCl solution. After adjustment to pH 5.0-5.5, the mixture is stirred for a further 4 h. The yellow crystals are then filtered  
 10 through a suction filter, washed with 5 % NaCl solution and dried *in vacuo* at 70°C.

Yield: 42.9 g

#### I.9. Compound of formula (108)

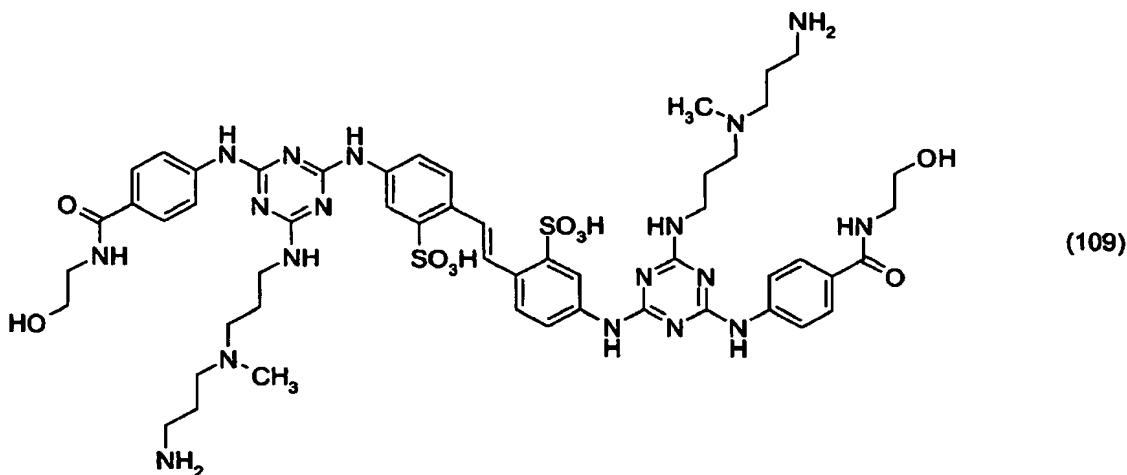


15

19.1 g (0.15 mol) of 1-(2-hydroxyethyl)-piperazine in 100 ml of water and 100 ml of dioxane are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 35.0 g (0.025 mol) of the intermediate of formula (105a) prepared according to Example I.6 are introduced. The yellow solution is stirred for 3 h at 86-88°C. After being  
 20 cooled to 70°C, the solution is then diluted with 50 ml of water and adjusted to pH 5.0 with 15 ml of conc. hydrochloric acid. After cooling to RT, the precipitate is filtered through a suction filter and washed with water. The filter cake is again suspended in 250 ml of water. After adjustment to pH 5, the mixture is stirred for a further 1 h at 70°C. The yellow crystals are then filtered through a suction filter, washed with water and dried *in vacuo* at 70°C.  
 25 Yield: 25.8 g (90 %)

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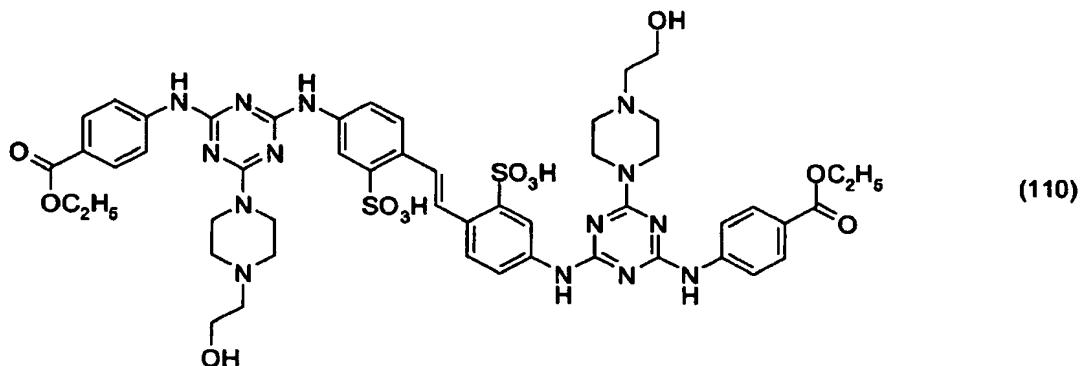
I.10. Compound of formula (109)



18.8 g (0.13 mol) of N,N-bis(3-aminopropyl)methylamine in 100 ml of water and 100 ml of dioxane are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 22.7 g (0.021 mol) of the intermediate of formula (105a) prepared according to Example I.6 are introduced. The yellow solution is stirred for 3 h at 86-88°C. After cooling to 70°C, the solution is then diluted with 120 ml of water and adjusted to pH 4.5 with 35 ml of conc. hydrochloric acid. After addition of 100 ml of acetone, the precipitate is filtered through a suction filter, washed with water and dried *in vacuo* at 70°C.

Yield: 28.7 g

I.11. Compound of formula (110)



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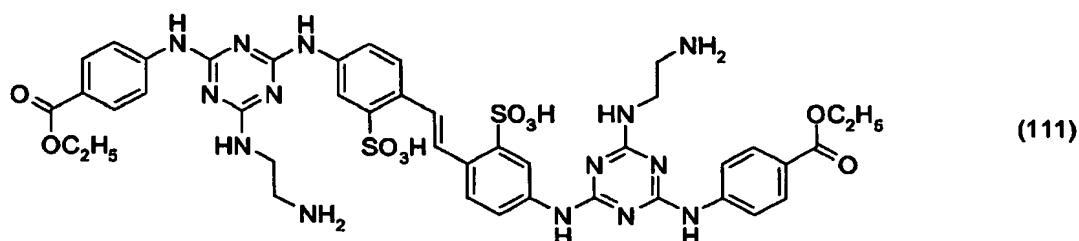
7.9 g (0.059 mol) of 1-(2-hydroxyethyl)-piperazine in 120 ml of water and 120 ml of dioxane are introduced into a 750 ml sulfonation flask equipped with a condenser and pH meter. At

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70-75°C, 25.0 g (0.025 mol) of the intermediate of formula (100a) prepared according to Example I.1 are introduced. The yellow solution is stirred for 3 h at 86-88°C. After being cooled to 70°C, the solution is adjusted to pH 4.5 with 10 ml of conc. hydrochloric acid. After being cooled to RT, the mixture is stirred for a further 1 h. The precipitate is filtered through a suction filter and washed three times with water. The filter cake is again suspended in 300 ml of water and the mixture is stirred at pH 5 for a further 1 h. The yellow crystals are then filtered through a suction filter, washed with water and dried *in vacuo* at 70°C.

5 Yield: 25.2 g (90 %)

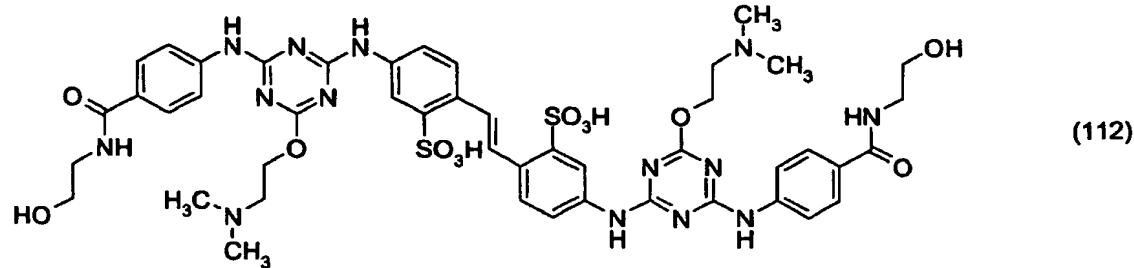
10 I.12. Compound of formula (111)



9.1 g (0.15 mol) of ethylenediamine in 120 ml of water and 120 ml of dioxane are introduced into a 750 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 25.4 g (0.025 mol) of the intermediate of formula (100a) prepared according to Example I.1 are introduced. The yellow solution is stirred for 4 h at 86-88°C. After being cooled to 70°C, the solution is adjusted to pH 4.5 with 18 ml of conc. hydrochloric acid and left to stand overnight. After the supernatant solution has been poured off, the residue is triturated in a mortar, filtered through a suction filter, washed with water and dried *in vacuo* at 70°C.

15 Yield: 22.6 g (93 %)

I.13. Compound of formula (112)



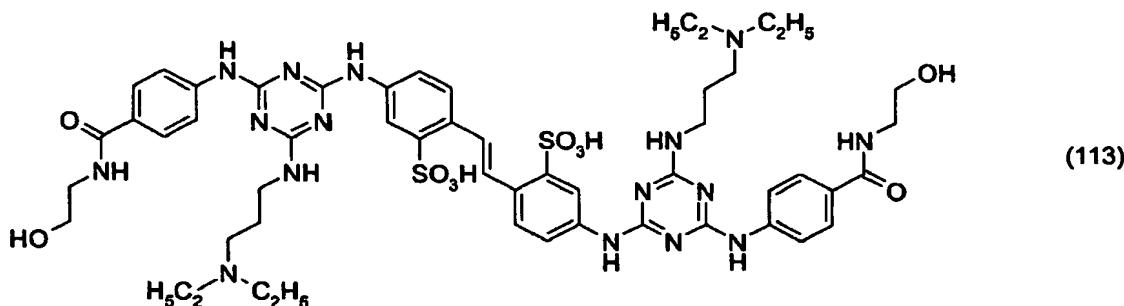
- 19 -

100 ml (1 mol) of 2-dimethylaminoethanol are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 30.0 g (0.03 mol) of the intermediate of formula (105a) are introduced. The yellow suspension is stirred for 1 h at 110-115°C. After being cooled to 90°C, the mixture is then diluted with 100 ml of water. The solution is

- 5 concentrated using a rotary evaporator, and the residue is dissolved in 150 ml of water. The pH is adjusted to 4.5 by addition of 20 ml of conc. hydrochloric acid. The precipitate is filtered through a suction filter, washed with water and dried *in vacuo* at 80°C.

Yield: 21.8 g (68 %)

10 I.14. Compound of formula (113)

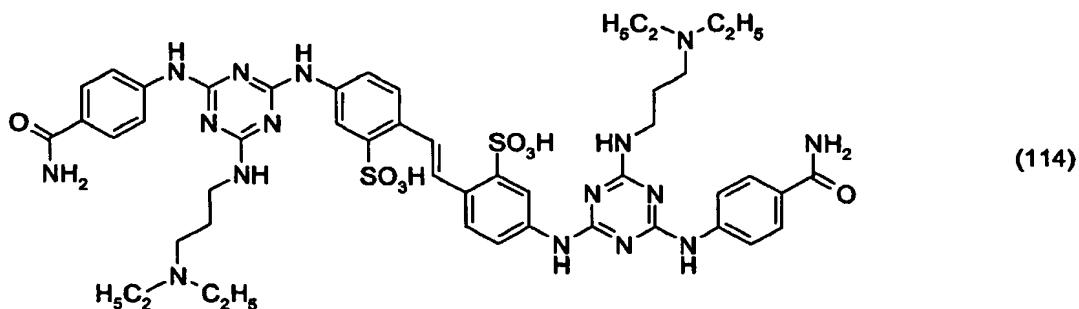


- 5.9 g (0.045 mol) of 3-diethylaminopropylamine in 70 ml of water are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter. At 70-75°C, 15.7 g (0.015 mol) of  
15 the intermediate of formula (105a) are introduced. The mixture is stirred for 4 h at 96-98°C and after cooling to 70°C is diluted with 100 ml of water. The pH is adjusted to 2.0 by addition of 7 ml of conc. hydrochloric acid. The precipitate is filtered through a suction filter and washed with a small amount of water. The filter cake is then suspended in 450 ml of water and stirred for 2 h at RT. The precipitate is filtered through a suction filter, washed with 2.5 %  
20 NaCl solution and dried *in vacuo* at 70°C.

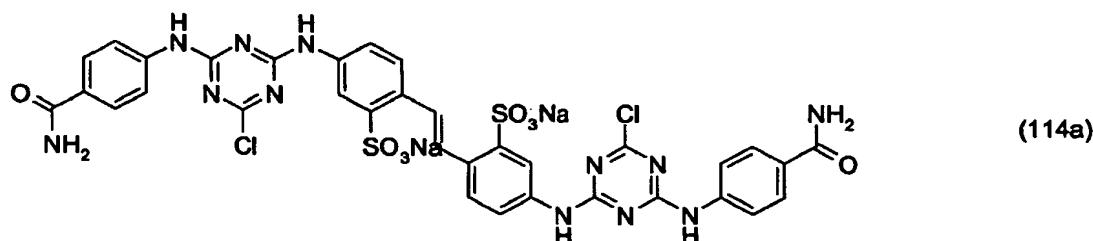
Yield: 16.8 g (98 %)

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I.15. Compound of formula (114)



(a) Intermediate of formula (114a)



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400 g of ice-water and 120 g (0.65 mol) of cyanuric chloride dissolved in 753 g of methyl ethyl ketone are introduced into a 2.5 litre flat-flanged flask equipped with a condenser, stirrer and pH meter. Then, in the course of 65 min, 990 ml of a 12 % solution of

10 4,4'-diaminostilbene-2,2'-disulfonic acid in soda water are slowly added dropwise at pH 4.5-5.0 so that no excess of disulfonic acid is formed. When the addition is complete, stirring is carried out for a further 10 min at an internal temperature of 5-10°C.

Then, in the course of 15 min, 90.3 g (0.65 mol) of 4-aminobenzamide are introduced at 10-20°C and pH 7.0-7.5 into the resulting yellow suspension.

15 The yellow suspension is then heated to 72°C in the course of one hour and stirred at that temperature for a further 2 h. After the solvent has been distilled off, the mixture is stirred for 4 h at 85°C and then left to stand overnight at RT. The crude product is filtered through a suction filter, washed with water and dried *in vacuo* at 80°C.

Yield: 327 g

20 Appearance: yellow crystals

(b) Compound of formula (114)

130 ml of water are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter and, at 70-75°C, 30.0 g (0.033 mol) of the intermediate of formula (114a) are intro-

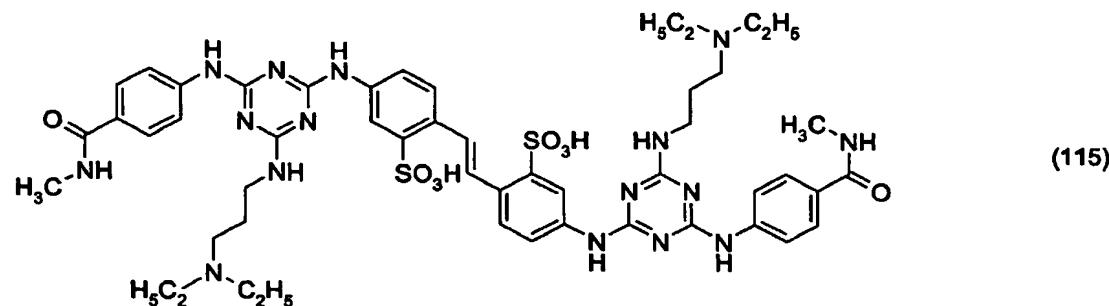
- 21 -

duced. 13.0 g (0.098 mol) of 1-amino-3-diethylaminopropane are then added dropwise. The yellow suspension so obtained is stirred for 8 h at 96-97°C and then left to stand overnight at RT. The pH is adjusted to 4.5 by addition of 12 ml of conc. hydrochloric acid. The precipitate is filtered through a suction filter, washed with 200 ml of water and then dried *in vacuo* at 5 80°C.

Yield: 30.0 g (86 %)

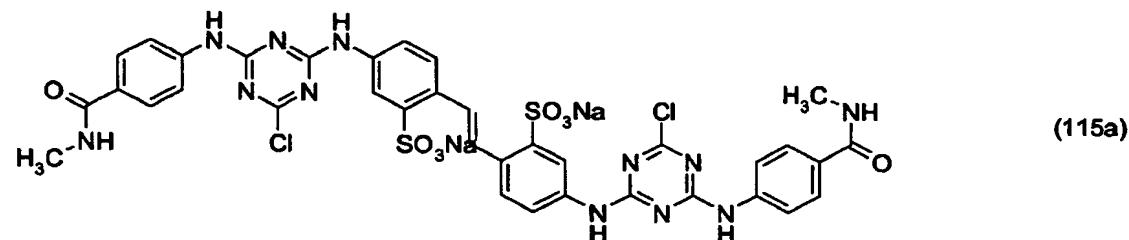
Appearance: beige crystals

#### I.16. Compound of formula (115)



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#### (a) Intermediate of formula (115a)



15 400 g of ice-water and 120 g (0.65 mol) of cyanuric chloride dissolved in 753 g of methyl ethyl ketone are introduced into a 2.5 litre flat-flanged flask equipped with a condenser, stirrer and pH meter. Then, in the course of 65 min, 977 ml of a 12 % solution of 4,4'-diaminostilbene-2,2'-disulfonic acid in soda water are slowly added dropwise at pH 4.5-5.0 so that no excess of disulfonic acid is formed. When the addition is complete, stirring is carried 20 out at an internal temperature of 5-10°C for a further 10 min.

Then, in the course of 15 min, 97.6 g (0.65 mol) of 4-amino-N-methylbenzamide are introduced at 10-20°C and pH 7.0-7.5 into the resulting yellow suspension.

The yellow suspension is then heated to 72°C in the course of one hour and stirred at that temperature for a further 2 h. After the solvent has been distilled off, a further 200 ml of water

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are added and the mixture is stirred for a further 1.5 h at 85°C. After cooling to 75°C, the crude product is filtered through a suction filter, washed with 2.5 % NaCl solution and dried *in vacuo* at 80°C.

Yield: 306.1 g

5    Appearance: yellow crystals

(b) Compound of formula (115)

130 ml of water are introduced into a 350 ml sulfonation flask equipped with a condenser and pH meter and, at 70°C, 30.0 g (0.030 mol) of the intermediate of formula (115a) are

10    introduced. 12.1 g (0.091 mol) of 1-amino-3-diethylaminopropane are then added dropwise. The yellow suspension so obtained is stirred for 4 h at 96-97°C. After cooling to 70°C, the pH is adjusted to 4.5 by addition of 8 ml of conc. hydrochloric acid. The precipitate is filtered off through a suction filter, washed with 200 ml of water and then dried *in vacuo* at 80°C.

Yield: 32.5 g (100 %)

15    Appearance: yellow crystals